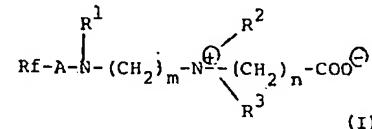


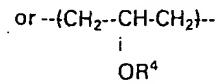
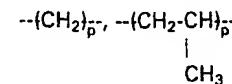
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 628 630 633 638 809 80Y  
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 None  
 (58) Field of search  
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## (54) Fluorine-containing betaine compounds

(57) A fluorine-containing betaine compound of the formula:



wherein Rf is a polyfluoroalkyl group having 3 to 21 carbon atoms, A is a group of the formula:

(wherein R<sup>4</sup> is a hydrogen atom or an acyl group having 2 or 3 carbon atoms and p is an integer of 1 to 5), R<sup>1</sup> is a hydrogen atom a C<sub>1</sub> to 20 alkyl group or a group of the formula: Rf-A-, R<sup>2</sup> and R<sup>3</sup> are each a hydrogen atom, a C<sub>1</sub> to 3 alkyl group or a C<sub>1</sub> to 3 hydroxy-alkyl group, m is an integer of 2 to 6 and n is an integer of 1 to 4, which is useful as an additive to a foam fire-extinguishing composition for polar organic liquids.

SEARCHED

## SPECIFICATION

## Fluorine-containing betaine compounds, and production and use thereof

5 The present invention relates to fluorine-containing betaine compounds, and to the production and use thereof. Particularly, it relates to novel fluorine-containing betaine compounds, a process for their preparation and their use as additives for foam fire-extinguishing agents, i.e. fire-fighting foaming agents, for polar organic liquids.

Conventional foam fire-extinguishing agents for polar organic liquids such as alcohols and ketones are 10 classified into the following two groups: (1) compositions comprising a partially hydrolyzed protein and (2) compositions comprising a synthetic surface active agent. An example of a composition of group (1) is partially hydrolyzed protein and, as an additive for improvement of liquid resistance and thermal resistance, a metal salt of an fatty acid dissolved in an aminoalcohol. Examples of compositions of group (2) are (i) a 15 foaming surface active agent and, as an additive for improvement of liquid resistance and thermal resistance a metal salt of a fatty acid dissolved in an aminoalcohol, and (ii) a foaming surface active agent and, as an additive, a water-soluble high molecular weight compound such as a sodium alginate.

Although both of these compositions possess fire-extinguishing ability, they suffer from the drawbacks mentioned below. In the composition of group (1), a water-insoluble metal salt of a fatty acid is dispersed in an aqueous solution of a partially hydrolyzed protein so that precipitation is apt to occur during storage for a 20 long time. When the composition is admixed with water at the site of a fire it must be used within several minutes, because otherwise a precipitate is formed in the water stream which causes a marked decrease in the fire-extinguishing ability of the composition. Further, pouring the foams onto the combustive liquid surface should be effected very quietly, or else a rapid disappearance of the foams is caused. In some polar 25 organic liquids such as alcohols, ketones, esters and others, an insoluble film is formed on the liquid surface and a relatively good effect can be obtained. But in case of amines, aldehydes, carboxylic acids and other similar polar organic liquids, foams are rapidly dissolved in the organic liquid and disappear because of the presence of the metal salt of a fatty acid, so that a desirable effect is not achieved.

In compositions of group (2) (i), precipitation during storage or after admixture is insignificant, but the fire-resistance is insufficient because a synthetic surface active agent is used as the main ingredient, and the 30 liquid resistance is inferior in comparison with compositions of group (1). In compositions of the group 2(ii), the formation is expected of an air-containing, floating layer in gel form having a good liquid resistance on the surface of the polar organic liquid by interaction between the organic liquid and a natural or synthetic high molecular weight compound. But, the effect is inferior in comparison with the compositions of groups 35 (1) and (2) (i). Since the reagent has a high viscosity, practical problems are caused by suction and an admixture.

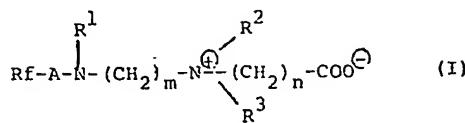
Furthermore, in all of the above-mentioned foam fire-extinguishing agents, sea water or stagnant water is often used for fire-extinguishing, so that precipitation is caused immediately after admixture because of the presence of metal salts contained in sea water or standing water, which results in a marked decrease in the fire-extinguishing effect.

40 Aqueous foam compositions comprising comprising water and fluoroalkyl group-containing compounds have been widely used for fire-extinguishing in oil fires i.e. of hydrocarbon fuels. For example, a foam fire-extinguishing agent comprising a derivative of fluorocarboxylic acid or fluorosulfonic acid is disclosed in Japanese Patent Publication No. 20080/1965. This composition is a foam fire-extinguishing agent usually called "light water" and may be employed for fire extinguishing in oil fires. It forms an aqueous film on the oil 45 surface to prevent evaporation of the inflammable vapour from the oil surface. Although this fire-extinguishing agent is thus effective for fire-extinguishing oil fires, an advantageous fire-extinguishing effect cannot be achieved with fires of polar organic liquids, because an aqueous film is not formed on the liquid surface.

Another type of known fire-extinguishing agent for oil fires is a protein foam fire-extinguishing agent, of 50 which a typical example is a composition comprising a protein fire-extinguishing compound and a fluorine containing surface active agent as an additive. For example, Japanese Patent Publication No. 21078/1972 discloses that, the incorporation of a small amount of perfluoroalkyl group-containing, water-soluble surface active agent into a hydrolyzed protein is effective in the enhancement of the fluidity and heat resistance of fire-extinguishing foams. In fact, all the water-soluble non-ionic or anionic surface active agents having a 55 perfluoroalkyl group as specifically exemplified therein produce good results with oil fires. However, none of them can produce foams of sufficient stability in fires due to polar organic liquids and are not practically usable for such fires. Furthermore, this publication teaches that the cationic surface active agents show a tendency to form precipitates in the fire-extinguishing composition and therefore that their use is not desirable.

60 We have now discovered that a specific group of novel fluorine-containing betaine compounds are extremely useful as additives for foam fire-extinguishing agents for polar organic liquids.

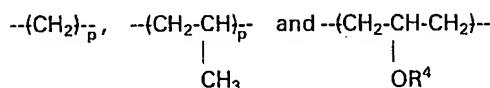
Accordingly, in one aspect of the present invention provides a fluorine-containing betaine compounds of the general formula:



5

wherein Rf is a polyfluoroalkyl group having from 3 to 21 carbon atoms, A is a group represented by one of the formulae:

10

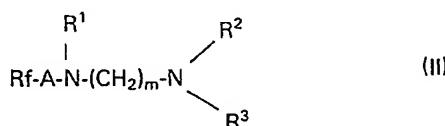


10

(wherein R<sup>4</sup> is a hydrogen atom or an acyl group having 2 or 3 carbon atoms and p is an integer of 1 to 5), R<sup>1</sup> is a hydrogen atom, an alkyl group having from 1 to 20 carbon atoms or a group of the formula: Rf-A-, R<sup>2</sup> and R<sup>3</sup> are each a hydrogen atom, an alkyl group having from 1 to 3 carbon atoms or hydroxy-alkyl group having from 1 to 3 carbon atoms, m is an integer of 2 to 6 and n is an integer of 1 to 4.

The fluorine-containing betaine compounds (I) of the present invention may be prepared by reacting a fluorine-containing diamine compound the general formula:

20



25

25

wherein Rf, A, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and m are each as defined above with a halogen-substituted alkanoic acid of the general formula:

30



30

wherein X is a halogen atom (except a fluorine atom) and n is as defined above or its salt, or an alkanolactone represented by the formula:

35



40

40

wherein q is an integer of 2 to 4.

When using the halogen-substituted alkanoic acid (III) or its salt, the reaction may be carried out, for example, by heating a mixture of an aqueous solution of an alkali metal salt of the halogen-substituted alkanoic acid (III) with the diamine compound (II), or a mixture of the halogen-substituted alkanoic acid (III) with an alkali metal hydroxide and the diamine compound (II), at 70 to 120°C for 1 to 5 hours with stirring. After removal of water, the resulting mixture is dissolved in an organic solvent, such as ethanol or ether, and then cooled. The product is, if necessary, recrystallized from suitable solvent so as to enhance the purity.

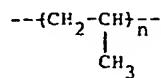
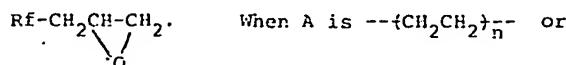
When using the alkanolactone (IV), either one of the diamine compound (II) and the alkanolactone (IV) is dissolved in a suitable solvent and the other is dropwise added thereto with stirring. The solvent may be a halogenated hydrocarbon (e.g. trichlorotrifluoroethane or methylene chloride), a ketone (e.g. acetone or methyl ethyl ketone), an ether (e.g. diethyl ether) or a nitrile (e.g. acetonitrile). These solvents may be used alone or in combination. The optimum reaction temperature is dependent upon the kinds of compounds (II) and (III) used as the starting materials. Generally a temperature of from 15 to 80°C is adopted. The reaction time is usually from 1 to 5 hours.

45

The diamine compound (II) as the starting material may be readily obtained by a conventional procedure. Namely, when A is  $-(\text{CH}_2\text{---CH(OH)CH}_2\text{)}_p$ , the compound (II) can be obtained by the reaction between the corresponding diamine compound and an epoxide of the formula:

50

55



reaction between the corresponding diamine compound and  $Rf-(CH_2CH_2)_n-I$  or  $Rf-(CH_2-CH)_n-I$ .

When  $R^4$  being an acyl group, the compound (II) in which A is  $-(CH_2CH(OH)CH_2)-$  is first obtained by the above mentioned procedure, and then this compound is acylated by treatment with a carboxylic anhydride. 5 Specific examples of the fluorine-containing betaine compound (I) thus prepared are given in Table 1.

Table 1

		M.P. (°C)
(1)	$  \begin{array}{c}  \text{OH} \\    \\  (\text{CF}_3)_2\text{CF}(\text{CF}_2)_6\text{CH}_2\text{CHCH}_2 \\    \quad \diagup \\  \text{N}-(\text{CH}_2)_3-\text{N}^{\oplus}-\text{CH}_2\text{CH}_2\text{COO}^{\ominus} \\    \quad \diagdown \\  \text{CH}_3 \quad \text{CH}_3  \end{array}  $	101
(2)	$  \begin{array}{c}  \text{OH} \\    \\  (\text{CF}_3)_2\text{CF}(\text{CF}_2)_6\text{CH}_2\text{CHCH}_2 \\    \quad \diagup \\  \text{N}-(\text{CH}_2)_3-\text{N}^{\oplus}-\text{CH}_2\text{CH}_2\text{COO}^{\ominus} \\    \quad \diagdown \\  \text{CH}_3 \quad \text{CH}_3 \\    \\  \text{OH}  \end{array}  $	96
(3)	$  \begin{array}{c}  \text{OH} \\    \\  (\text{CF}_3)_2\text{CF}(\text{CF}_2)_6\text{CH}_2\text{CH}_2 \\    \quad \diagup \\  \text{N}-(\text{CH}_2)_3-\text{N}^{\oplus}-\text{CH}_2\text{CH}_2\text{COO}^{\ominus} \\    \quad \diagdown \\  \text{CH}_3 \quad \text{CH}_3  \end{array}  $	103
(4)	$  \begin{array}{c}  \text{OH} \\    \\  (\text{CF}_3)_2\text{CF}(\text{CF}_2)_6\text{CH}_2\text{CH}_2 \\    \quad \diagup \\  \text{N}-(\text{CH}_2)_3-\text{N}^{\oplus}-\text{CH}_2\text{CH}_2\text{COO}^{\ominus} \\    \quad \diagdown \\  \text{CH}_3 \quad \text{CH}_3 \\    \\  (\text{CF}_3)_2\text{CF}(\text{CF}_2)_6\text{CH}_2\text{CH}_2  \end{array}  $	98
(5)	$  \begin{array}{c}  \text{OH} \\    \\  \text{F}(\text{CF}_2)_8\text{CH}_2\text{CHCH}_2 \\    \quad \diagup \\  \text{N}-(\text{CH}_2)_2-\text{N}^{\oplus}-\text{CH}_2\text{CH}_2\text{COO}^{\ominus} \\    \quad \diagdown \\  \text{CH}_3 \quad \text{CH}_3  \end{array}  $	93
(6)	$  \begin{array}{c}  \text{OH} \\    \\  (\text{CF}_3)_2\text{CF}(\text{CF}_2)_6\text{CH}_2\text{CH}_2 \\    \quad \diagup \\  \text{N}-(\text{CH}_2)_2-\text{N}^{\oplus}-\text{CH}_2\text{CH}_2\text{COO}^{\ominus} \\    \quad \diagdown \\  \text{CH}_3 \quad \text{CH}_3  \end{array}  $	97
(7)	$  \begin{array}{c}  \text{OH} \\    \\  \text{F}(\text{CF}_2)_8\text{CH}_2\text{CH}_2 \\    \quad \diagup \\  \text{N}-(\text{CH}_2)_2-\text{N}^{\oplus}-\text{CH}_2\text{CH}_2\text{COO}^{\ominus} \\    \quad \diagdown \\  \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5  \end{array}  $	95
(8)	$  \begin{array}{c}  \text{OH} \\    \\  (\text{CF}_3)_2\text{CF}(\text{CF}_2)_6\text{CH}_2\text{CHCH}_2 \\    \quad \diagup \\  \text{N}-(\text{CH}_2)_3-\text{N}^{\oplus}-\text{CH}_2\text{CH}_2\text{COO}^{\ominus} \\    \quad \diagdown \\  \text{CH}_3 \quad \text{CH}_3  \end{array}  $	90

		<u>M.P. (°C)</u>
(9)		40
5	$  \begin{array}{c}  \text{O} \\  \parallel \\  \text{O-C-CH}_3 \\    \\  (\text{CF}_3)_2\text{CF}(\text{CF}_2)_6\text{CH}_2\text{CHCH}_2 \\    \\  \text{N-}(\text{CH}_2)_3\text{-N}^{\oplus}\text{-CH}_2\text{CH}_2\text{COO}^{\ominus} \\    \\  \text{CH}_3 \\    \\  \text{CH}_3  \end{array}  $	5
10		10
(10)		107
15	$  \begin{array}{c}  \text{OH} \\    \\  \text{F}(\text{CF}_2)_8\text{CH}_2\text{CHCH}_2 \\    \\  \text{N-}(\text{CH}_2)_2\text{-N}^{\oplus}\text{-CH}_2\text{CH}_2\text{COO}^{\ominus} \\    \\  \text{F}(\text{CF}_2)_8\text{CH}_2\text{CHCH}_2 \\    \\  \text{OH}  \end{array}  $	15

20 In general, the combustibility or reactivity of polar organic liquids such as alcohols and ketones is  
 dependent upon the polarity, the types of functional groups, the number of carbon atoms, etc. Therefore, the  
 fire-extinguishing effect of a fire-extinguishing agent varies depending upon the type of the polar organic  
 liquid which is to be extinguished and none of the conventional foam fire-extinguishing agents can produce  
 a sufficient fire-extinguishing effect with a variety of polar organic liquids. By using the fluorine-containing  
 25 betaine compound (I) of the invention, a satisfactory fire-extinguishing effect can be obtained for a wide  
 range of polar organic liquids such as alcohols, ketones, esters, ethers, aldehydes, carboxylic acids and  
 amines. The fluorine-containing betaine compound (I) has no undesirable influence upon the foaming ability  
 of hydrolyzed proteins and synthetic surface active agents as the main ingredients of the foam  
 fire-extinguishing agents. When it is incorporated into the organic liquid of a fire-extinguishing agent  
 30 containing such a main ingredient the formation of a precipitate does not occur even after storage for a long  
 time, unlike the conventional fire-extinguishing agents, so that the fire-extinguishing effect is thus  
 maintained.

When, for example, the fluorine-containing betaine compound (I) is incorporated into a partially  
 hydrolyzed protein, it is usually used in an amount of from 0.1 to 30% by weight, preferably from 1 to 10% by  
 35 weight, of the original liquid to of a protein foaming agent (3% type or 6% type). Into the resultant mixture,  
 other additives such as a surface active agent and a freezing-preventing agent may be further incorporated if  
 necessary. The composition so obtained is usually diluted with water and employed according to  
 conventional techniques.

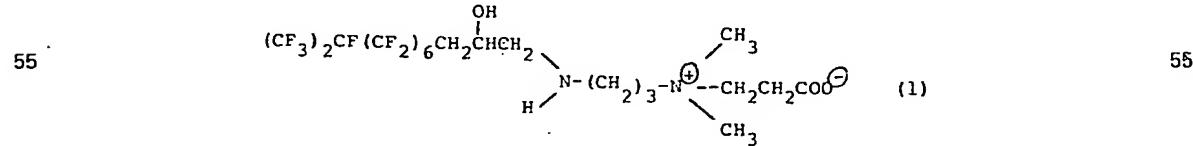
When the foaming agent is a synthetic surface active agent, such as sodium lauryl sulfate, the  
 40 fluorine-containing betaine compound (I) may be used almost in the same proportion to the original liquid of  
 the foaming agent as above to afford a composition useful as a foam fire-extinguishing agent for polar  
 organic liquids.

The fluorine-containing betaine compound (I) is very useful as an additive not only for the foam  
 fire-extinguishing agents for polar organic liquids but also for foam fire-extinguishing agents for oily fires.  
 45 Owing to its specific surface activity, the betaine compound (I) is further utilizable for various uses such as  
 additives for cleaners, waxes, haze-preventing agents and various etching agents and evaporation-inhibiting  
 agents.

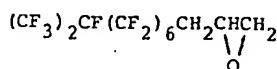
The present invention will be further described with reference to the following Examples and Comparative  
 Examples.

50

*Example 1*

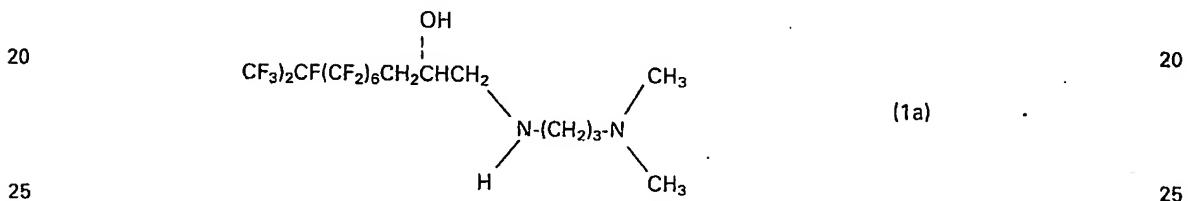


60 (A) In a 350 ml-volume three-necked flask equipped with a reflux condenser, a stirring apparatus and a  
 dropping funnel, ethanol (150 ml) and N,N-dimethylaminopropylamine (102 g, 1.0 mol) were charged, and  
 while stirring at 60°C in a water bath kept at 60°C, an epoxide compound represented by the formula:



5 was dropwise added thereto through the dropping funnel. After the addition of this epoxide (52.6 g, 0.10 mol) in 90 minutes, stirring was continued for further 90 minutes under heating. The reaction mixture was subjected to programmed temperature gas chromatographic analysis (column, Silicone SE-30, 3m; column temperature, temperature-elevation of 4°C/min from 100°C whereby it was confirmed that the starting epoxide was completely consumed, and a peak of the known substance of the formula:  $(CF_3)_2CF(CF_2)_5-$  10  $CH=CH-CH_2OH$  was observed, in addition to the objective compound as the main product.

The whole reaction mixture was poured into an evaporator, and the unreacted amine and the said by-product were eliminated at 120°C under a pressure of 10 mmHg to obtain a product with a gas chromatographic purity of 97% (61 g). The thus obtained main object product was subjected to a GC-MS analysis, and from the obtained data which was shown below, this product was proved to be the compound 15 of the formula:



Apparatus: Shimadzu LKB-9000 type

Conditions: Gas-Chro column SE-30, 3 m

30 column temperature, elevated with a rate  
of 4°C/min from 100°C  
ionization voltage, 70 eV

Main peaks (M/e):	Ion	
35 629	$(M + H)^+$ ( $M$ = parent ion)	35
590	$(M - 2F)^+$	
556	$Rf-CH_2-CH(OH)CH_2-NHCH_3^+$	

Main peaks (m/e):	Ion	
40 58	$(\text{CH}_3)_2\text{NCH}_2^+$	40
85	$(\text{CH}_3)_2\text{NC}_3\text{H}_5^+$	

(B) In a 300 ml-volume three-necked flask equipped with a reflux condenser, a stirring apparatus and a cropping funnel, a mixture of trichlorotrifluoroethane and acetonitrile (50/50 by volume) (100 ml) and 45  $\beta$ -propiolacetone (3.2 g, 0.044 mol) were charged, and while stirring at 30°C in a water bath, the compound (1a) which was diluted 6 times by weight with the said solvent mixture of trichlorotrifluoroethane/acetonitrile was dropwise added thereto. After the addition of this compound (25.1 g, 0.04 mol) in 120 minutes, stirring was continued for further 90 minutes. After the reaction, the solid precipitate was collected by filtration, washed well with a solvent mixture of trichlorotrifluoroethane/acetonitrile (50/50 by volume) and dried in 50 vacuum to obtain a product (18 g).

By the conventional bromophenol blue test and methylene blue test, this product was confirmed to possess a property as a betaine type amphoteric active agent.

In the IR absorptive spectrum, the strong absorption at  $1830\text{ cm}^{-1}$  which was seen in the starting  $\beta$ -propiol- and derived from stretching vibration of  $\text{C}=\text{O}$  disappeared, and strong absorptions at  $1590\text{ cm}^{-1}(-\text{COO}^-)$  and at  $1100 - 1300\text{ cm}^{-1}(-\text{CF})$  and other absorptions were observed.

The result of the elementary analysis correspond well to the theoretical values as shown below:

	<i>Found</i>	<i>Calcd.</i>	
60 C	34.1 (%)	34.3 (%)	60
H	3.2	3.3	
F	51.2	51.6	
N	4.1	4.0	
O	(7.4) <sup>1)</sup>	6.8	
65 Sum	100.0	100.0	65

Note: \*) Value obtained by subtracting the sum of C,H,F and N from 100.

**Example 2**

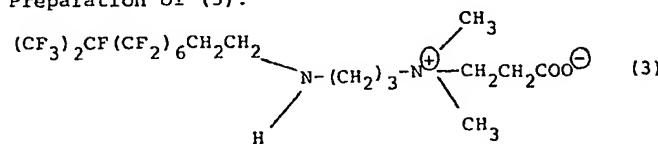
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Example 2

5

Preparation of (3):

10



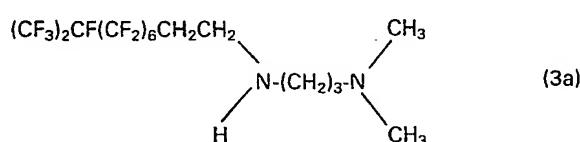
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(A) In a 100 ml-volume three-necked flask equipped with a reflux condenser, a stirring apparatus and thermometer, an iodine compound of the formula:  $(\text{CF}_3)_2\text{CF}(\text{CF}_2)_6\text{CH}_2\text{CH}_2\text{I}$  (18.7 g, 0.03 mol) and 15 N,N-dimethylaminopropylamine (30.6 g, 0.3 mol) were charged, and the contents were stirred for 4 hours in a water bath kept at 90°C. By the gas chromatographic analysis, it was confirmed that the starting iodine compound was consumed by the reaction almost completely.

After the reaction, the reaction mixture was poured into a separating funnel and washed well with a 2% by weight NaOH solution and then with water several times. The washed mixture was then poured into an 20 evaporator, and the unreacted amine and other substances were eliminated at 120°C under a pressure of 10 mmHg to obtain a product with a gas chromatographic purity of 97.5% (10.5 g).

From the data obtained by the GC-MS analysis under the same condition as in Example 1, the product was proved to be the compound of the formula:

25



25

30

30

Main peaks

35	579	(m/e): Ion $(M-F)^+$ (M = parent ion)
	558	$(M - 2HF)^+$
	101	$(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}^+$

35

(B) In a 100 ml-volume three-necked flask equipped with a reflux condenser, a stirring apparatus and a dropping funnel, the compound (3a) obtained in (A) (9.0 g, 0.015 mol) and acetone (50. ml) were charged, and 40 while stirring at 30°C in a water bath,  $\beta$ -propiolactone which was diluted 5 times by weight with acetone was dropwise added thereto. After the addition of  $\beta$ -propiolactone (1.45 g, 0.02 mol) in 30 minutes, stirring was continued for further 60 minutes. By gas chromatographic analysis, it was confirmed that the starting material (3a) was consumed by the reaction almost completely.

40

After the reaction, the reaction mixture was poured into an evaporator to eliminate acetone and the residue 45 was purified by recrystallization from a solvent mixture of ethanol/n-hexane (30-70 by volume. The solid product isolated from the solvent was dried in vacuum to obtain a product (5.0g). By the bromophenol blue test and methylene blue test as in Example 1, this product was confirmed to possess a property as a betaine type amphoteric active agent. In the IR absorption spectrum, the strong absorption at  $1830 \text{ cm}^{-1}$  ( $>\text{C}=\text{O}$ ) seen in -propiolactone disappeared, and strong absorptions at  $1590 \text{ CM}^{-1}$  ( $-\text{COO}^-$ ) and at  $1100 - 1300 \text{ cm}^{-1}$  50 ( $-\text{CF}$ ) and other absorptions were observed.

50

The result of the elementary analysis corresponded well to the theoretical values as shown below:

	Found	Calcd	
55 C	33.8 (%)	34.0 (%)	55
H	3.2	3.1	
F	53.4	53.9	
N	4.3	4.2	
O	(5.3)*	4.8	
60 Sum	100.0	100.0	60

Note: \*) Value obtained by subtracting the sum of C,H,F and N from 100.

### Example 3

**A foam fire-extinguishing composition was prepared from the following components:**

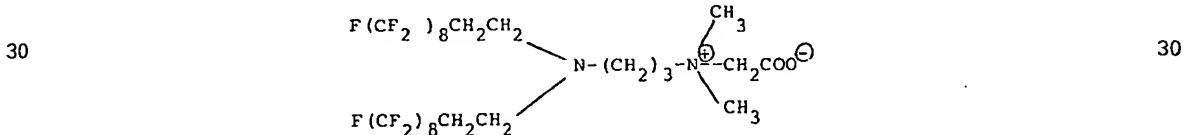
		Part(s) (by weight)	
5	Protein foam fire-extinguishing agent of 3% type (comprising hydrolyzed protein and additives such as iron salts)	3.0	5
10	Surface active agent (the fluorine-containing betaine compound (1) shown in Table 1)	0.1	10
15	Water	96.9	15

This composition (100 ml) was charged into a 1 liter volume polyethylene vessel and the content was stirred for 2 minutes under a speed of 2,000 rpm by the aid of a stirring wing inserted into the vessel to prepare foam. The volume of the produced foam was read from the volume graduations on the vessel. The 20 foam (20 ml) was taken out and placed on the surface of methanol or acetone (70 ml) contained in a 100 ml volume beaker, and measurement of time by a stop watch was started.

The amounts of remaining foam after 10 and 20 minutes were determined by macroscopic measurement. The results are shown in Table 3.

### *Examples 4 to 7*

25 A foam fire-extinguishing composition was prepared from the same components as in Example 3 but using as the surface active agent the fluorine containing betaine compound (3), (2) or (7) shown in Table 1 or the compound of the formula:



35 The same test for foam stability was carried out. The results are shown in Table 3. 35

### **Comparative Examples 1 to 10**

A foam fire-extinguishing composition was prepared from the same components as in Example 3 but using no surface active agent or using a conventional fluorine-containing surface active agent shown in Table 2, and the same test for foam stability was carried out. The results are shown in Table 3.

Table 2

Comparative Example No.	Surface active agent
1	Not used
2	$\text{F}(\text{CF}_2)_8\text{SO}_2-\overset{\text{C}_3\text{H}_7}{\underset{ }{\text{N}}}-\text{CH}_2\text{COOK}$
3	$\text{F}(\text{CF}_2)_7\text{COONH}_4$
4	$\text{F}(\text{CF}_2)_8\text{OC}_6\text{H}_4\text{SO}_3\text{K}$
5	$\text{F}(\text{CF}_2)_8\text{SO}_2-\overset{\text{C}_3\text{H}_7}{\underset{ }{\text{N}}}-\text{CH}_2\text{CH}_2\text{O})_{10}\text{H}$
6	$\text{F}(\text{CF}_2)_8\text{SO}_2-\overset{\text{C}_3\text{H}_7}{\underset{ }{\text{N}}}-\text{CH}_2\text{CH}_2\text{O})_{10}\text{SO}_3\text{K}$
7	$\text{F}(\text{CF}_2)_8\text{SO}_2-\overset{\text{H}}{\underset{ }{\text{N}}}-\text{CH}_2\text{CH}_2\text{O})_3-\overset{\oplus}{\text{N}}(\text{CH}_3)_3\text{I}^\ominus$
8	$\text{F}(\text{CF}_2)_8\text{CO}_2-\overset{\text{H}}{\underset{ }{\text{N}}}-\text{CH}_2\text{CH}_2\text{O})_3-\overset{\oplus}{\text{N}}(\text{CH}_3)_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{CH}_2\text{CH}_2\text{COO}^\ominus}}$
9	$\text{F}(\text{CF}_2)_3\text{CO}-\overset{\text{H}}{\underset{ }{\text{N}}}-\text{CH}_2\text{CH}_2\text{O})_3-\overset{\oplus}{\text{N}}(\text{CH}_3)_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{CH}_2\text{CH}_2\text{COO}^\ominus}}$
10	$\text{F}(\text{CF}_2)_8\text{CH}_2\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{N}^\oplus}}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{CH}_2\text{CH}_2\text{COO}^\ominus}}$

Table 3

Kind of foam fire-extinguishing agent	Multiplication of foaming <sup>1)</sup>	Polar solvent	Stability of foam	
			After 10 minutes	After 20 minutes
Example 3	9	Acetone	90 % remaining	70 % remaining
		Methanol	90 % remaining	80 % remaining
Example 4	9	Acetone	80 % remaining	60 % remaining
		Methanol	80 % remaining	70 % remaining
Example 5	9	Acetone	90 % remaining	70 % remaining
		Methanol	90 % remaining	70 % remaining

Example 6	8	Acetone	80 % remaining	50 % remaining
		Methanol	80 % remaining	60 % remaining
Example 7	8	Acetone	90 % remaining	70 % remaining
		Methanol	90 % remaining	70 % remaining
Comparative Example 1	9	Acetone	disappear-ing within 5 seconds	-
		Methanol	-	-
Comparative Example 2	8	Acetone	disappear-ing within 10 - 12 seconds	-
		Methanol	-	-
Comparative Example 3	9	Acetone	Disappear-ing within 5 - 7 seconds	-
		Methanol	-	-
Comparative Example 4	9	Acetone	Disappear-ing within 5 - 7 seconds	-
		Methanol	-	-
Comparative Example 5	3	Acetone	Disappear-ing within 5 seconds	-
		Methanol	-	-
Comparative Example 6	3	Acetone	Disappear-ing within 5 seconds	-
		Methanol	-	-
Comparative Example 7	8	Acetone	Disappear-ing within 5 - 7 seconds	-
		Methanol	-	-
Comparative Example 8	9	Acetone	10 % remaining	5 % remaining
		Methanol	20 % remaining	10 % remaining
Comparative Example 9	9	Acetone	20 % remaining	10 % remaining
		Methanol	20 % remaining	10 % remaining
Comparative Example 10	8	Acetone	Disappear-ing within 5 - 7 seconds	-
		Methanol	-	-

Note: \*) Multiplication of foaming = volume of foam (ml)/100 (ml)

### Example 8

Using the compositions prepared in Example 3, Example 6, Comparative Example 1, Comparative Example 2 and Comparative Example 7, the following test was carried out.

Example 2 and Comparative Example 3, the following procedure was adopted. Into a vat (0.45 m × 0.45 m × 0.3 m; 0.2 m<sup>2</sup>), methanol (20 liters; height of liquid surface, 20 cm) was poured, and the vat was ignited. After 5 minutes, the said composition was continuously ejected through a foaming nozzle (1 lit/min/5/kg/cm<sup>2</sup>) for 5 minutes to produce foam. Measurement of time was started simultaneously with the initiation of the ejection, and the time required for inhibition of fire by the foam spreading on the combustive surface of methanol and the time required for complete fire-extinguishing were recorded as the combustion-inhibiting time and the fire-extinguishing time, respectively. After completion of the continuous foaming for 5 minutes, the model was allowed to stand still for 15 minutes. Then, flame of a torch stick was made to come near the liquid surface to effect recombustion test (torch test). The results are shown in Table 4.

The same test was repeated as above but using another foaming nozzle (0.5 lit/min/5 kg/cm<sup>2</sup>). The results are shown in Table 5.

Table 4

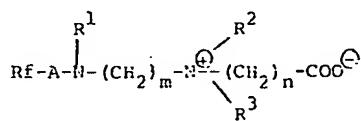
	Composition	Example 3	Example 6	Comparative Example 1	Comparative Example 2	Comparative Example 7	
20	Inhibiting time	40 sec.	50 sec.	not inhibited	not inhibited	1 min. and 50 sec.	20
25	Fire-extinguishing time	1 min.	1 min. and 20 sec.	not extinguished	not extinguished	2 min. and 20 sec.	25
	Torch test	not ignited	not ignited	not determined	not determined	not ignited	

Table 5

Composition	Example 3	Example 6	Comparative Example 1	Comparative Example 2	Comparative Example 7	
35 Inhibiting time	2 min.	2 min. and 20 seconds	not inhibited	not inhibited	not inhibited	35
40 Fire-extinguishing time	2 min. and 40 sec.	3 min. and 10 sec.	not extinguished	not extinguished	not extinguished	40
Torch test	not ignited	not ignited	not determined	not determined	not determined	

## CLAIMS

1. A fluorine-containing betaine compound of the general formula:



wherein Rf is a polyfluoroalkyl group having from 3 to 21 carbon atoms, A is a group of the formula:

$$\text{--}(\text{CH}_2)\text{--}\overset{\circ}{\text{P}}\text{, } \text{--}(\text{CH}_2\text{--CH})\text{--}\overset{\circ}{\text{P}}\text{ or } \text{--}(\text{CH}_2\text{--CH--CH}_2)\text{--}$$

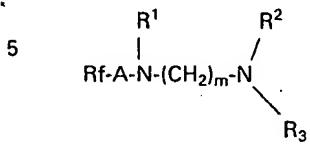
$\begin{array}{c} | \\ \text{CH}_3 \end{array}$ 

 $\begin{array}{c} | \\ \text{OR}^4 \end{array}$

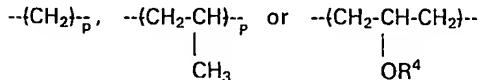
(wherein  $R^4$  is a hydrogen atom or an acyl group having 2 or 3 carbon atoms and  $p$  is an integer of 1 to 5),  $R^1$  is a hydrogen atom, an alkyl group having from 1 to 20 carbon atoms or a group of the formula:  $Rf-A$ ,  $R^2$  and  $R^3$  are each a hydrogen atom, an alkyl group having from 1 to 3 carbon atoms or a hydroxyalkyl group having from 1 to 3 carbon atoms,  $m$  is an integer of 2 to 6 and  $n$  is an integer of 1 to 4.

65 having from 1 to 3 carbon atoms, m is an integer of 2 to 6 and n is an integer of 1 to 4. 65

2. A compound of the formula (1) given in Table 1.
3. A fluorine-containing betaine compound of the general formula:



10 wherein Rf is a polyfluoroalkyl group having from 3 to 21 carbon atoms, A is a group of the formula: 10

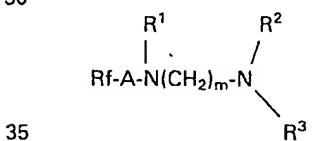


(wherein R<sup>4</sup> is a hydrogen atom or an acyl group having 2 or 3 carbon atoms and p is an integer of 1 to 5), R<sup>1</sup> is a hydrogen atom, an alkyl group having from 1 to 20 carbon atoms or a group of the formula: Rf-A, R<sup>2</sup> and R<sup>3</sup> are each a hydrogen atom, an alkyl group having from 1 to 3 carbon atoms or a hydroxy-alkyl group having from 1 to 3 carbon atoms, m is an integer of 2 to 6 and n is an integer of 1 to 4.

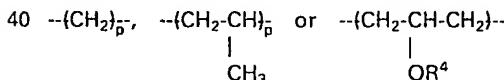
Having from 1 to 3 carbon atoms, m is an integer of 2 to 5 and n is an integer of 1 to 4.

20 4. A compound of the formula (3) as given in Table 1. 20  
 5. A compound of the formula (4) as given in Table 1.  
 6. A compound of the formula (5) as given in Table 1.  
 7. A compound of the formula (6) as given in Table 1.  
 8. A compound of the formula (7) as given in Table 1.

25 9. A compound of the formula (8) as given in Table 1. 25  
 10. A compound of the formula (9) as given in Table 1.  
 11. A compound of the formula (10) as given in Table 1.  
 12. A process for the preparation of a fluorine-containing betaine compounds as claimed in claim 1 which process comprises reacting a fluorine-containing diamine compound of the formula:



wherein Rf is a polyfluoroalkyl group having from 3 to 21 carbon atoms, A is a group of the formula:



(wherein R<sup>4</sup> is a hydrogen atom or an acyl group having 2 or 3 carbon atoms and p is an integer of 1 to 5), R<sup>1</sup> is a hydrogen atom, an alkyl group having from 1 to 20 carbon atoms or a group of the formula: Rf-A, R<sup>2</sup> and R<sup>3</sup> are each a hydrogen atom, an alkyl group having from 1 to 3 carbon atoms or a hydroxyalkyl group having from 1 to 3 carbon atoms and m is an integer of 2 to 6, with a halogen-substituted alcanoic acid having 2 to 5 carbon atoms or its salt or an alkanolactone having 3 to 5 carbon atoms.

50 Having 2 to 6 carbon atoms in its side chain and substituents having 3 to 5 carbon atoms.

50 13. A process as claimed in claim 12 substantially as hereinbefore described with reference to Example 1 or Example 2.

14. A compound as claimed in claim 1 whenever prepared by a process as claimed in claim 12 or claim 13.

55 15. A fire-extinguishing composition for polar organic liquids which comprises an aqueous solution of a partially hydrolyzed protein and, as an additive contained therein, a fluorine-containing betaine compound as claimed in any one of claims 1 to 11, or claim 14.

55 16. A fire-extinguishing composition as claimed in claim 15 substantially as hereinbefore described with reference to any one of Examples 3 to 7.